Original article

Kinetic modeling of CuO chlorination with C\textsubscript{2}Cl\textsubscript{4}

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A B S T R A C T

Chlorinating roasting is a well-known process devoted mainly for the extraction of metals as volatile chlorides from oxidized minerals and residues. Experience has shown that the use of a gaseous chlorinating agent, Cl\textsubscript{2}, for example, and the incorporation of a reducing agent, charcoal, for example, stimulate, respectively the kinetics and thermodynamics of the desired reactions. In this scenario, organo-chlorinated molecules, such as, CCl\textsubscript{4} and C\textsubscript{2}Cl\textsubscript{4}, appear as potential candidates for Cl\textsubscript{2} replacement, as they can be easily volatilized and bear in the same molecule the chlorinating and reducing agents. In order to support reactor sizing, however, reliable kinetic data is needed, which are scarce regarding both mentioned chlorinating agents. In present work, chlorination of pure CuO samples with diluted C\textsubscript{2}Cl\textsubscript{4} (P(C\textsubscript{2}Cl\textsubscript{4}) = 0.0307 atm) has been quantitatively appreciated in the range between 923 and 1173 K. The kinetic data were modeled according to the Shrinking-Core model (SCM) and a quantitative agreement between experimental and calculated data has been found for all temperatures. Finally, a global activation energy of 117.9 ± 10 kJ/mol has been determined, which is close to earlier literature values for similar systems. A significant reduction of the form factor with temperature (3 to 1.5) has been detected, which, can be correlated to the partial sintering of the remaining CuO crystals.

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1. Introduction

Chlorinating roasting is usually devoted to extraction and the separation of one or more metallic elements from multi-constituent oxidized raw materials, such as, mineral concentrates [1], tailings [2] and slags [3], through formation of volatile chlorides. These processes are generally performed at high temperatures (973–1273 K), whereas gaseous chlorine (Cl\textsubscript{2}) reacts with the oxides usually in the presence of some sort of reducing agent, charcoal, for example, to promote

the thermodynamic driving force for the desired chlorinating reactions [4]. In this way, zirconium and titanium have been extracted from Zr\textsubscript{O\textsubscript{2}} and FeTiO\textsubscript{3} concentrated ores [5]. However, both from economic and environmental perspectives, it is natural to look for processes based on alternative chlorinating agents. Chlorine gas is very aggressive and should be handled with care. Moreover, through substitution of Cl\textsubscript{2} by less reactive molecules, such as, for example, CCl\textsubscript{4} or C\textsubscript{2}Cl\textsubscript{4}, the plant operation costs could be significantly reduced regarding the equipment for both storage and transport. In this context, alternative agents that bear chlorine and carbon in the same molecule, and also that can be easily volatilized, such as, for example, CCl\textsubscript{4} or C\textsubscript{2}Cl\textsubscript{4}, seem to be interesting candidates for Cl\textsubscript{2} replacement.

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On what touches modeling of gas–solid kinetic data, the Shrinking–Core model (SCM) has gained considerable acceptance in literature, and has been applied with success for describing experimental data in reaction systems of varying nature [6–8]. In the work of Túnez et al. [6], pure Ir2O3 samples have been chlorinated under Cl2 atmosphere in the temperature range between 773 and 923 K. The obtained thermogravimetric data has been modeled according to SCM, global activation energy and reaction order being respectively equal to 125.5 kJ/mol and 0.91. Also, for the entire temperature range, the form factor (f) has shown to be equal to 2.5. Yang and Hlavacek [7] also employed thermogravimetry for studying the chlorination of TiO2, both as rutile and anatase, under N2–CO–Cl2 atmospheres, in the temperature range between 1073 and 1273 K. The kinetic data has been modeled according to SCM and global activation energies have shown to be equal to 74 and 54 kJ/mol, for rutile and anatase, respectively.

On what touches the global reaction order, the values found for Cl2 and CO have shown to be equal to 1 and 0.83, for rutile, and 1 and 0.86 for anatase, the form factor being in all cases set equal to 3. In the work of Kanari et al. [8], Fe2O3 particles were exposed to a Cl2 atmosphere and the chlorination studied in a thermogravimetric balance in the range between 873 and 1273 K. The authors employed the SCM and evidenced in the mentioned temperature range two global activation energy values, 180 ± 4 kJ/mol at lower temperatures (873–1148 K) with form factor equal to 3, and 74 ± 3 kJ/mol at higher temperatures (1173–1273 K) with a form factor equal to one. The authors claim that at higher temperatures control is associated to the diffusion of the Cl2 molecules to the surface of the oxide particles, whereas at lower temperatures the chemical reaction at surface should control the kinetic behavior of the system.

In the work of Pomiroti et al. [9], chlorination of pure Eu2O3 samples with Cl2 between 423 and 1223 K was studied. According to the authors, only at lower temperatures (573–673 K) kinetics should be controlled by the chemical reaction of Cl2 at the particles surface. The isothermal thermogravimetric data have been modeled with the Johnson–Mehl–Avrami equation, which bears a close mathematical relation with the one found for SCM. The global activation energy and reaction order have proven to be respectively equal to 114 ± 8 kJ/mol and 0.54, the gas flow rate varying between $5 \times 10^{-4}$ and $2 \times 10^{-3}$ L/s. Bosco et al. [10] have studied the chlorination of Nd2O3 samples under Cl2 atmosphere through thermogravimetric analysis in the range between 585 K and 748 K. For temperatures lower than 748 K, the authors evidenced chemical control, and the isothermal data described with the Johnson–Mehl–Avrami model. The global activation energy and reaction order in respect to Cl2 have shown to be respectively equal to 161 ± 4 kJ/mol and 0.39, the gas flow rate fixed at $3.6 \times 10^{-4}$ L/s.

Jena et al. [11] studied the chlorination of pure ZrO2 crystals under the presence diluted C2Cl4–N2 atmospheres, through exposing the zirconia particles to chlorinating media in a tubular oven under constant flux. The experiments have been conducted for a C2Cl4 partial pressure of 0.6 atm and temperatures varying in the range between 700 and 750 K. For the temperature interval between 700 and 725 K, the authors evidenced that the kinetics is described by SCM, with a form factor equal to 3, and global activation energy of 154 kJ/mol. For the interval between 725 and 750 K however, kinetics was modelled with the Langmuir–Richelwood isotherm, with an activation energy of 54 kJ/mol. The authors associate this much lower activation energy with the dissociation of the CCl4 molecules over the ZrO2 surface. Mink et al. [12] have studied the chlorination of V2O5 and TiO2 samples under CCl4 atmosphere through thermogravimetry in the temperature range between 450 to 550 K for V2O5 and 770 to 920 K for TiO2. In both cases, the authors conclude that the chlorination is preceded by the reactive adsorption of CCl4 molecules, with possible formation of COCl2, as detected through mass spectrometry for the V2O5 sample. Through evaluation of initial reaction rates, apparent activation energies of 75 kJ/mol and 118 ± 7 kJ/mol, have been determined for V2O5 and TiO2, respectively.

Pap et al. [13] studied the chlorination of pure Al2O3 samples through thermogravimetric experiments under the presence of N2–CCl4 atmosphere of 2.1 kPa CCl4 partial pressure, and temperature varying in the range between 650 and 820 K. The authors employed the kinetic data for determining the initial chlorination rate, and modeled this information through the conception that chlorination involves three specific moments, the first one represented by the adsorption of CCl4 and covering of Al2O3 surface, dissociation of CCl4 and transferring of chlorine atoms to the solid, and finally formation and volatilization of AlCl3 molecules. The activation energies for the two last steps have been determined in different temperature ranges through Arrhenius plots. Regarding the transfer of chlorine atoms to the oxide crystal structure, values equal to 209 kJ/mol and 105 kJ/mol have been determined in the ranges between 650–720 K and 720–820 K. On what touches the formation of AlCl3 molecules, apparent activation energies of much lower magnitude have been determined at the same temperature ranges, and have proven to be, respectively, equal to 163 kJ/mol and 81 kJ/mol. According to the authors, the reduction evidenced in both cases for the calculated apparent activation energies at temperatures higher than 720 K should be associated to the influence of diffusional effects.

As presented before, although a few works are found in literature regarding the use of CCl4 as an alternative chlorinating agent, the same is not true in the case of C2Cl4. Until the present date, the only paper found in literature regarding the chlorinating action of C2Cl4 is due to the work of Bertóti et al. [14]. In this work, thermogravimetric analysis has been employed for studying the chlorination of pure Al2O3 samples in N2–C2Cl4 atmosphere in the range between 973 and 1073 K, and C2Cl4 partial pressure of 1.6 kPa. Through Arrhenius plots based on the evaluation of initial chlorination rates, an apparent activation energy of 141 kJ/mol has been determined. A similar analysis based on the Langmuir–Hischelwood isotherm, which assumes the adsorption of C2Cl4 and subsequent dissociation of these molecules in C and Cl at the crystal surface, an apparent energy of 133 kJ/mol was calculated. Based on these results, the authors claim that on what touches the experimental conditions employed, the controlling step for the chlorination reaction should be associated with the dissociation of the chlorinating agent over the oxide surface. Finally, in a previous work of our research group [15], it was demonstrated that CuO...
chlorination with diluted $\text{C}_2\text{Cl}_4$ at 1123 K is supported both through thermodynamic simulations and experiments.

In the present work, chlorination kinetics of CuO samples with $\text{C}_2\text{Cl}_4$ has been experimentally investigated in the range between 923 and 1173 K, and the resulting kinetic data described by the SCM. In this approach, it is considered that kinetics is controlled by interface chemical reaction between $\text{C}_2\text{Cl}_4$ and the oxide particles. The kinetic constant values obtained have then been used for the calculation of the process global activation energy.

2. Methods

2.1. Oxide synthesis

For the synthesis of the desired CuO particles, a similar strategy as used before [15] have been employed. The CuO samples were synthesized from controlled masses of analytical grade Cu(NO$_3$)$_2$·$\text{H}_2\text{O}$. The pure nitrate was heated up to 623 ± 10 K during 40 min to remove most part of the nitrogen initially present as gaseous NO$_2$. Additionally, in order to ensure the absence of residual nitrates, samples were submitted to an additional heat treatment during 30 min in a muffle furnace at 773 ± 5 K. The proposed synthesis methodologically the production of oxide samples of high nanostructured content, whereas CuO was the sole oxide present [15].

2.2. Chlorination tests

The chlorination tests were conducted on a line consisting of a distilled water bath with digital temperature control, where a container with liquid $\text{C}_2\text{Cl}_4$ of analytical grade was maintained at thermal equilibrium at 297 ± 2 K, the N$_2$ flux was fixed at $6.15 \times 10^{-3}$ L/s, resulting in a total gas flow of $5.86 \times 10^{-3}$ L/s. Under such conditions, $\text{C}_2\text{Cl}_4$ partial pressure at the reactor entrance has proven to be equal to 0.0307 atm [15]. The sample, comprising one gram of pure CuO, is then inserted into a quartz tubular fixed bed reactor, previously set at the desired reaction temperature. However, before admission of the gaseous mixture carrying the chlorinating agent of interest ($\text{C}_2\text{Cl}_4$), samples were exposed to an atmosphere of pure N$_2$ ($6.15 \times 10^{-3}$ L/s) during 10 min, in order to guarantee that the measured mass loss during chlorination was associated entirely with the chlorination process under study. After this time interval, the crucible is removed from the oven and the initial mass determined ($m_0$). The sample is next reinserted into the furnace under a N$_2$ + $\text{C}_2\text{Cl}_4$ flow, and the remaining mass measured as a function of time (m) through use of a digital balance with precision of ±0.001 mg, reaction temperature varying in the range between 923 ± 5 K and 1173 ± 5 K. The oxide conversion was evaluated according to Eq. (1).

\[
x = \left( \frac{m_0 - m}{m_0} \right) \]

2.3. Kinetic modeling

For the kinetic modeling of the measured conversion, the SCM (Eq. (2)) has been employed [7].

\[
kt = 1 - (1 - x)^{1/f} = g(x)
\] (2)

where k, x and f represent, respectively, the kinetic constant, oxide conversion and the form factor, which bears a relation to the geometry of the particles.

In this theoretical approach, chemical control is assumed, which is in agreement with the physical nature of the process under study, since, as said before, the produced copper oxide should be associated with significant nanostructured content [15], enhancing the contact area between sample and atmosphere, thereby reducing any possible diffusional limitations. Another factor that reduces the chance of any diffusional effects over the kinetic data is associated with the formation of only volatile chlorides. This guarantees that at any moment the particle surface can be free for direct contact with new $\text{C}_2\text{Cl}_4$ molecules.

The determination of the kinetic constant based on the experimental data has been performed through construction of a Matlab code, which minimizes the least squares sum of the differences between experimental and calculated conversion values based on a simplex algorithm, k and f being allowed to simultaneously vary. However, on what touches the form factor (f), a maximum value of three has been set, which is consistent to a size reduction in three independent space dimensions. For one or two dimensional contractions, f should be respectively equal to one and two [7]. With the k value obtained at each reaction temperature, the global process activation energy ($E_a$) can be determined by using Eq. (3), k$_0$ representing the pre-exponential factor from the Arrhenius equation and R the universal gas constant.

\[
\ln k = \ln k_0 - \frac{E_a}{RT}
\] (3)

2.4. Characterization

In order to study possible microstructural changes regarding the remaining CuO particles, one of the chlorinated samples (30 min, 1123 K) has been characterized through SEM, with a HITASHI tabletop microscope, model TM 3000, working at 15 kV, and contrast based on back-scattered electrons.

3. Results and discussion

3.1. Thermodynamic appreciation

In the temperature range of interest for the present article (923–1173 K), data on Figs. 1 and 2, which depict the system speciation under varying $\text{C}_2\text{Cl}_4$ to N$_2$ molar ratio (R$_c$) at 923 and 1173 K, corroborates earlier data [15], and shows that, at both temperatures, thermodynamic viability can be expected even under high $\text{C}_2\text{Cl}_4$ dilution (low R$_c$ values). For the calculations the software Thermocalc has been used and the Gibbs energy models extracted from the SSUB3 data-base [16].
For both temperatures and $R_c$ values lower than 0.025, no Cl$_2$ should be detected. At such conditions, most of the C$_2$Cl$_4$ supplied reacts with CuO, thereby generating volatile chlorides (Cu$_3$Cl$_3$ and Cu$_2$Cl$_2$). For higher $R_c$ values, Cl$_2$ is formed through C$_2$Cl$_4$ excess thermal decomposition (Eq. (4)).

$$C_2Cl_4(g) \rightarrow 2C(s) + 2Cl_2(g) \quad (4)$$

It is also interesting to observe that at each temperature there is a maximum $R_c$ value for which graphite starts to take part in equilibrium, which should be equal to approximately 0.039 at 923 K and 0.05 at 1173 K.

Between 0.025 and the mentioned maximum value, graphite generated by decomposition of the chlorinating agent should be converted to CO according to the Bourdoux reaction (C + CO$_2$ = 2CO). This explains the behavior depicted in Fig. 3, whereas at both temperatures the CO mol fraction achieves a maximum value.

Finally, it is worthwhile to mention that the $R_c$ value established during the experiments performed ($R_c = 0.032$) should indeed lie in the range, whereas no graphite is deposited over the chlorinated sample, which, together with the fact that sole volatile chlorides are formed, supports the use of Eq. (1) for computing the CuO conversion at each temperature studied.
3.2. Kinetic modeling

According to the optimization results, SCM (Eq. (2)) was able to describe the experimental data in a quantitative level (Figs. 4–7). As expected, the kinetic constant is a function of temperature, and reduces as reaction temperature achieves lower values. Moreover, the study evidences that the form factor was constant and equal to three at 923 K and 1023 K, but assumes a value close to 1.5 for the data obtained at 1123 and 1173 K (Table 1). The appreciable form factor reduction with temperature rise should be associated with some changing regarding the geometry of the oxide particles.

The observed variation of $f$ could be explained by the partial sintering of the powder. As a result, the porosity of the oxide bed reduces and the contraction, which at lower temperatures involves all three spatial directions ($f = 3$), becomes limited, resulting in a much lower form factor. This conclusion is supported by SEM data (Fig. 8), which suggests the partial sintering of the remaining CuO crystals after chlorination at 1123 K during 30 min.

It should be pointed out, that the observed reduction of the form factor with rising reaction temperature (3 to 1.5) has already been reported regarding the use of SCM for describing kinetic data in the Fe$_2$O$_3$–Cl$_2$–N$_2$ system in the range between 1173 and 1273 K [8], and, as said before, could be explained through a partial sintering of the remaining oxide particles.

3.3. Global activation energy evaluation

After implementation of Eq. (3) to the optimized values for the kinetic constant determined at each temperature (923, 1023, 1123 and 1173 K), a quantitative agreement was achieved (Fig. 9), with a R$^2$ value of 95.7%, and a final least squares sum of 0.268, both giving support to the modeling quality.

The linear regression of data presented in Fig. 9 resulted in an activation energy of 117.9 ± 10 kJ/mol, of magnitude consistent with earlier literature values for similar systems [6,8–13]. Much lower energy values are usually observed, when either diffusional effects are present [11], or when in the reaction system considered, gaseous molecules containing carbon are available, CO, for example, and which can work as reductive agents during the process [7].

It is interesting to observe that the global activation energy calculated in the present work lies in the range reported by Berthóti et al. [13] for the chlorination of Al$_2$O$_3$ with CCl$_4$, considering as limiting step the dissociation of CCl$_4$ molecules over the Al$_2$O$_3$ crystals, and concomitant transfer of chlorine atoms to the crystal at the exposed surface (163–81 kJ/mol). A similar limiting step was also considered for explaining the kinetics of Al$_2$O$_3$ chlorination under N$_2$–C$_2$Cl$_4$ atmospheres, resulting in apparent energies varying in the range 133–141 kJ/mol [14], as well as in the case of chlorination of TiO$_2$ samples under the presence of CCl$_4$ [12], whereas

Fig. 4 – (a) Conversion ($x$) as a function of time at 923 K. (b) Data linearization according to the SC model.

Fig. 5 – (a) Conversion ($x$) as a function of time at 1023 K. (b) Linearization according to the SC model.
an activation energy of 118.4 ± 10 kJ/mol has been found. The agreement between the present apparent activation energy and the values determined for the chlorination of Al₂O₃ [13,14] and TiO₂ [12] suggests that also in the present case, control should be associated to some chemical reaction step in the mechanism involving the C₂Cl₄ molecules dissociation. – As both TiO₂ and Al₂O₃ have much higher stability in comparison with CuO (Fig. 10), the agreement between the present apparent activation energy and the values determined for Al₂O₃ [13,14] and TiO₂ [12] chlorination suggests that, also in the present case, control should be associated with some reaction step involving C₂Cl₄ molecules dissociation over the oxide particles surface.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>k</th>
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<tbody>
<tr>
<td>923</td>
<td>0.0014</td>
<td>3</td>
</tr>
<tr>
<td>1023</td>
<td>0.0042</td>
<td>3</td>
</tr>
<tr>
<td>1123</td>
<td>0.0288</td>
<td>1.479</td>
</tr>
<tr>
<td>1173</td>
<td>0.0278</td>
<td>1.553</td>
</tr>
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</table>

Fig. 6 – (a) Conversion (x) as a function of time at 1123 K. (b) Linearization according to the SC model.

Fig. 7 – (a) Conversion (x) as a function of time at 1173 K. (b) Linearization according to the SC model.

Fig. 8 – SEM image of CuO sample after chlorination at 1123 K for 30 min.
After data analysis, it was observed a significant reduction of the form factor between from 3.0 (923 and 1023 K) to a value close to 1.5 (1023 and 1173 K), which could be explained based on the possible sintering of the remaining CuO particles, as evidenced through SEM data (Fig. 8).

**Conflicts of interest**

The authors declare no conflict of interest.

**REFERENCES**


